

Isotopic characteristics and the origin of the coalbed methane in Tunlan minefield, Xishan coalfield, Taiyuan

Few studies can be found on the origin of coalbed methane in Tunlan minefield of Xishan coalfield, Taiyuan, which leads to incomprehensive understanding of the overall characteristics of coalbed methane genesis in Xishan coalfield. Based on the chemical composition and isotope test data of 6 gas wells in Xishan coalfield, this paper discusses the origin of coalbed methane. The results show that the average volume fractions of methane, ethane, nitrogen, carbon dioxide and argon are 89.93%, 0.03%, 6.64%, 0.30% and 0.12% respectively. and the values of carbon isotope and hydrogen isotope are -43.85%~-41.3% and -238.27%~-222.45%. carbon dioxide isotope value is -12.8%~-6.0%. Data of chemical composition and isotopic test in Tunlan minefield shows that the coalbed methane has undergone secondary transformation, which is due to coal degradation. Secondary biogenic methane has been formed, which is the mixed genetic coalbed methane, and the secondary biogenic gas accounts for about 35%.

Keywords: Carbon isotope, coalbed methane, secondary biogenic gas, thermal degradation, Xishan coalfield.

1. Introduction

The chemical and isotopic compositions of coalbed gas are the main contents of coalbed gas geochemical investigation, and the carbon isotopic composition has become an effective index to determine the origins of the coalbed gas and to understand the distribution law. Some studies have shown that the carbon isotope value of methane of coalbed gas becomes heavier with the coal evolution [1,2]. Actually, the coalbed gas carbon isotopic composition varies greatly due to the influence of multiple factors including the desorption-diffusion-migration effect, thermal evolution degree, groundwater dynamic conditions and microbial effects. The structure geometry influences the distribution of

coalbed gas [3], and the tectonic uplift of the coal seam leads to the desorption-diffusion-migration effect, which results in the larger value of the carbon isotope of coalbed methane. And the value becomes heavier with the increase of depth, accompanied by zoning phenomenon in the plane [4]. The isotopic differentiation effect of the coalbed gas formation under the thermodynamic mechanism leads to the heavier methane carbon isotope with the greater maximum reflectance of coal vitrinite and coal seam depth [5-7]. The experimental data confirms that the flowing water lightens the methane carbon isotope [8], so the coalfields with strong hydrodynamic force contain a small amount of coalbed gas, where the methane carbon isotope is relatively light [9]. The carbon isotopes of microbial coalbed methane are generally lighter; the primary biogenic gases usually appear in the low-rank coals, and the secondary biogases occur in coal rocks with high thermal evolution and even in anthracite [10-11]. The microbiogenic gases can even constitute the main reason for the sustained and stable production of coalbed gas [12]. Compared to the conventional natural gas, the coalbed gas composition and its carbon isotopic composition are differently affected by the secondary action with different influencing effects. The latter is determined in the geologic period with the highest evolutionary level, which can reflect the thermal evolution process of coal seam [13,14]. At present, few studies touch upon the relationship between origins of methane and carbon dioxide of coalbed gas in the Taiyuan Xishan coalfield, so it is necessary to study the origins of coalbed gas in this area.

The author takes the gas production in the wellhead of Tunlan minefield in the central of Xishan coalfield as research object (Fig.1(a) and (b)). Through testing and analyzing the chemical components and carbon isotopes of coalbed methane, the characteristics and the causes of formation of the carbon isotope of coal seam methane and carbon dioxide in this area are studied and discussed.

2. Regional geological background

The Taiyuan Xishan coalfield is located in the middle of the Shanxi transitional block of the North China plate, the West

Messrs. Jianjun Li and Hui Chang, School of Science, North University of China, 030 051, Taiyuan, Shanxi, Junlong Zhang and Yaoyao Cai, Institute of Earthquake Science, China Earthquake Administration, 100 036, Beijing, Baoyu Wang, Shanxi Jincheng Anthracite Mining Group Co. Ltd., 048 006, Jincheng, Shanxi, China. Corresponding author e-mail: zhjulo_2002@163.com and ljcc@163.com

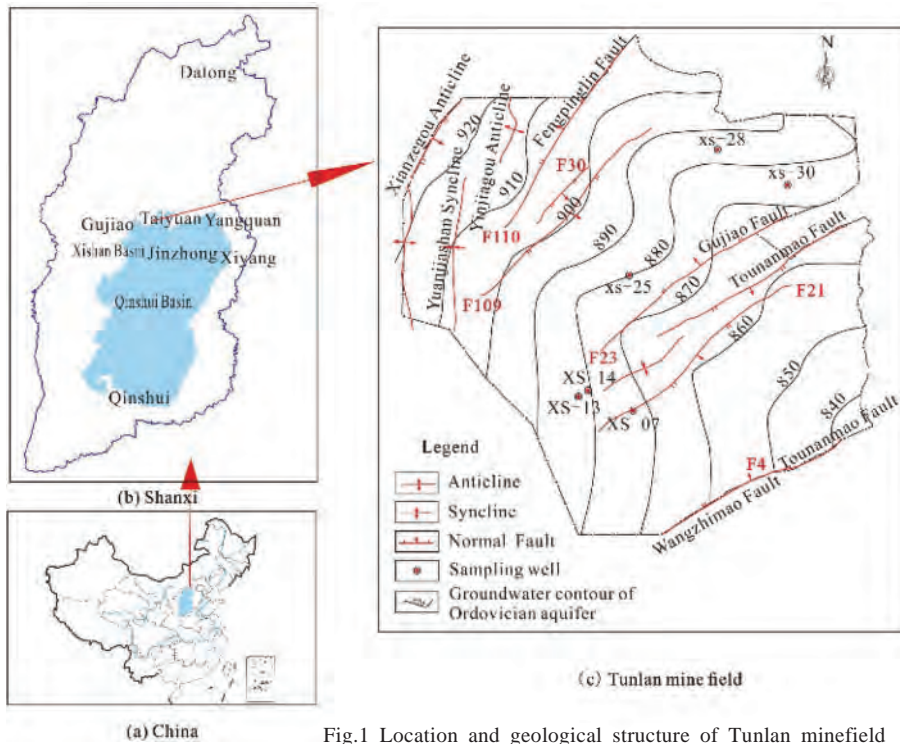


Fig.1 Location and geological structure of Tunlan minefield

Wing of the Lvliang-Taihang fault block. The northern boundary of the coalfield is the west part of Yuxian-Yangqu fold belt. Its east and south end is adjacent to the Taiyuan basin, and Lvliang uplift is in its west. The whole area is controlled by regional tectonic belts including the east-west structure, the north-south structure, the north-north east to north east trending structure and other composite structures. The north-south structure significantly affects the structure of the mining area. The tectonic evolution process of the West Mountain in Taiyuan is divided into 5 stages[15-17]: (1) Late Carboniferous to early Permian: slow settling stage with an average sedimentation rate of no more than 14m/Ma.(2) Late Permian to late Triassic: rapid subsidence stage with an average settlement rate of 95m/Ma; the first hydrocarbon generation period. (3) Early Jurassic to Middle Jurassic; first uplift and then settlement. (4) Late Jurassic to the early Cretaceous; experienced a strong Yanshan magmatic activity; the second hydrocarbon generation period. (5) Since the late Cretaceous, the strata were constantly eroded and the buried depth of coal seam decreased continuously.

Tunlan minefield is located in the northwest of the Xishan coalfield. The strata extends in the direction of NW30°~60°, inclining to SW with and inclination angle 5°~10°. It is a wave-like monocline structure from NNE to SSW, with relatively developed small undulating folds. Surface faults appear in group and are in the form of horst (Fig.1(c)). The main coal bearing strata are upper Carboniferous Taiyuan formation and lower Permian Shanxi formation, which contain 18 coal layers. The average thickness of coal measures is about 158.50m, and the average thickness of coal seam is 15.70m, with a coal

bearing coefficient of 10%. The extraction of coalbed methane mainly occurs in Taiyuan formation No.8 and No.9 and Shanxi formation No.2, in which rich coal, coking coal, lean coal are mainly contained, and thickness of No.9 is small with less stability. The changing law of coal quality is obvious. Vertically, the degree of metamorphism from top to bottom is gradually deepened; horizontally, the degree of metamorphism gradually deepens from the northwest to the southeast.

The groundwater related to coalbed methane in the Tunlan minefield mainly belongs to Shanxi formation sandstone fissure water bearing rock group and the Taiyuan formation sandstone thin layer limestone fissure bearing water rock group. The Shanxi formation sandstone fissure water bearing rock group has relatively good ability of

water bearing and water permeability, which weakens as depth increases. K_2 is the main water bearing layer in the Taiyuan formation sandstone thin layer limestone fissure bearing water rock group, with high water content and strong hydrodynamic force. The hydraulic connection between aquifers is weak, as shown in Fig.2.

3. Samples and test methods

3.1 SAMPLE COLLECTION

The gas samples used in this experiment are collected by the drainage gas-collection method, and the sampling water is deionized saturated salt water sealed in glass bottles.

The sampling point of coalbed methane is in Tunlan minefield, Xishan of Taiyuan City. XS-28 and XS-30 are in the east-central part of the minefield. XS-25 is in the central part. XS-13?XS-14 and XS-07 are in the southwestern part of the well field. XS-13 and XS-30 are only extracted from coalbeds No.2+ No.8. The rest of holes are extracted from coalbeds No.2+ No.8+ No.9. six groups of samples are collected from coalbed gas well with six holes. Each group contains two gas samples as contrasts. Coalbed methane is primarily extracted from No.8 coalbed in Taiyuan formation. Every gas sample contains 200~500mL. Relevant tests are conducted on chemical constituents and isotope composition in the lab.

3.2 TEST METHODS AND CONDITIONS

The chemical composition and isotope testing of coalbed gas are completed at the Key Laboratory of Lanzhou Oil and Gas Resources Research Center, Institute of Geology and Geophysics, Chinese Academy of Sciences. The chemical

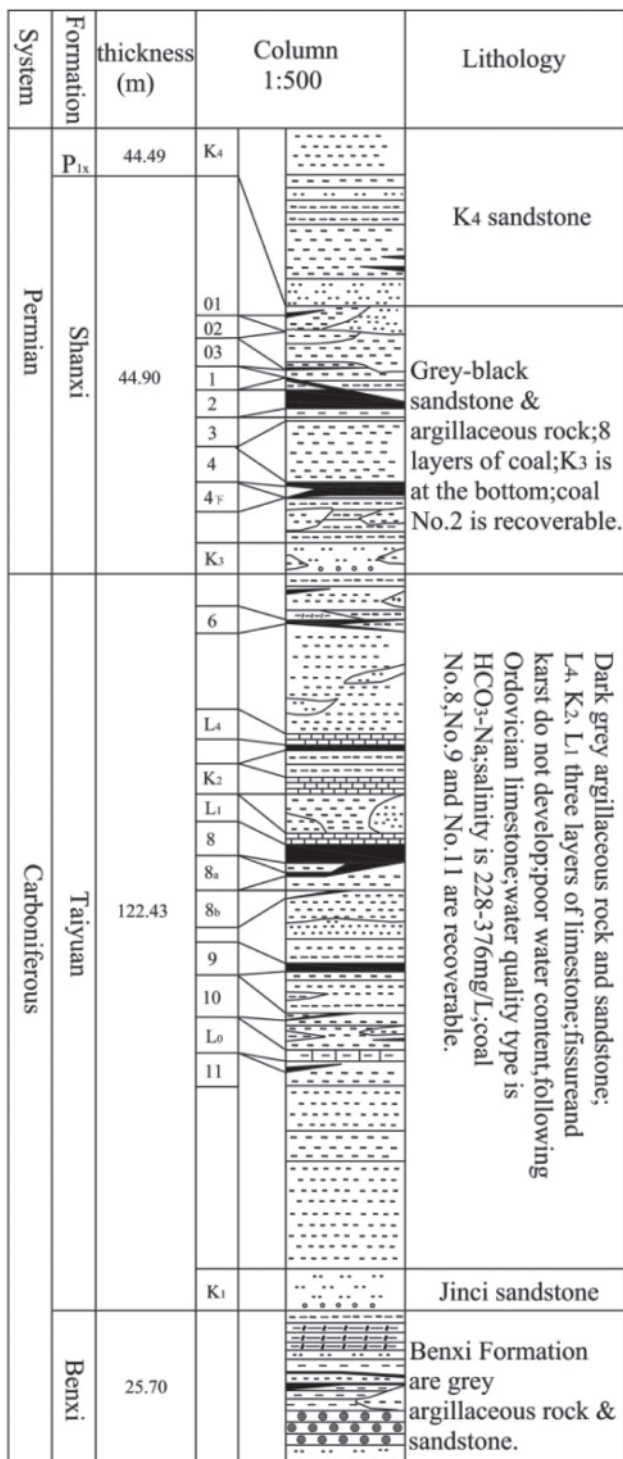


Fig.2 The stratigraphic histogram of the Tunlan minefield

composition of coalbed gas is tested by the large-scale gas isotope mass spectrometer (type: MAT 271, manufactured by Feenigan, Germany) with the Faraday cup for signal reception and the ionization source of electron bombardment.

The carbon isotope of methane and carbon dioxide and the hydrogen isotope of methane are tested and analyzed on

the stable isotope analysis system, which is mainly composed of the gas chromatography (GC) and isotope ratio mass spectrometer, referred to as "GC-IRMS" analysis system. The chromatograph type is Agilent 6890, and the chromatographic column type is CP-Carbobond (manufactured by Varian Company, 25cm in length, 0.53mm in inner diameter, 10μm in film thickness). The inlet split ratio is 3:1, and the temperature is 200°C. The temperature is programmed to stay at 40°C for 5 min and rise to 240 °C at the rate of 15°C/min, at which point the temperature is maintained for 10 min. Helium is the carrier gas (purity > 99.999 %), whose flow rate is 5mL/min. The type of the stable isotope mass spectrometer is Deltaplus XP (manufactured by Thermo Fisher Scientific, USA), of which the oxidation reaction temperature is 920°C, the ion source filament emission current is 1.5mA and the electron energy is 120eV. The accuracy of the carbon and hydrogen isotope test is ± 0.2%~± 1%. The test results are shown in Table 1.

Tests on chemical constituents and isotope composition of coalbed methane are completed in the key laboratory of Lanzhou Research Center of Oil & Gas Resources, Institute of Geology and Geophysics. Test results are shown in Table.1.

4. Geochemical characteristics of coalbed methane

4.1 CHARACTERISTICS OF GEOCHEMICAL COMPONENTS OF COALBED METHANE

In Tunlan minefield, CH₄ is the main component of coalbed methane. The volume fraction ranges from 86.19% to 93.52%. Average content is 89.93%. The content of ethane is small, ranging from 0.02%~0.05%. Average content is 0.03%. Non-hydrocarbon gases include nitrogen, carbon dioxide and argon. Volume contents are 4.54%~8.98%, 0.21%~0.34% and 0.07%~0.16% respectively. Average contents are 6.64%, 0.30% and 0.12% respectively. The dry coefficient values are greater than 0.99, which indicates that they are extremely dry gases judging from the chemical components with the CDMI of 0.24 ~ 0.38 %.

Positive correlation exists between N₂ content and δ¹³C(CH₄). N₂ content is high. δ¹³C(CH₄) is also high (Fig.3). in addition, negative correlation exists between N₂ and CH₄ content (Fig.4). It shows that N₂ in the air dissolves into the coal reservoir through underground water. N₂ content is high in coalbed methane. N₂ is the main component of the atmosphere, and its content reaches 78.08%. It can dissolve into surface water and permeate to the underground coal seam. Besides, chemical property is not active, so it can exist stably. Coalbed gas in this region is methane. The infiltration capacity is different at different sections of the atmosphere. As a result, linear decline and growth are shown between N₂ and CH₄ contents in the coalbed gas. Hence, according to the N₂ content, preservation conditions of coalbed gas can also be inferred [18]. Among the test samples taken from Tunlan minefield of Xishan in Taiyuan, other than XS-14 and XS-13, N₂ contents in the rest of samples are greater than 5%.

TABLE 1: GEOCHEMICAL COMPOSITION DATA OF COALBED METHANE IN TUNLAN MINEFIELD OF XISHAN COALFIELD

Well no.	Composition /%					Dryness coefficient $c_1/(c_1+c_2)$	CDMI / %	δ-value of isotope /%			Coal seam	Depth of no 15 coal seam /m
	CH ₄	C ₂ H ₆	CO ₂	N ₂	Ar			δ ¹³ C(CH ₄)	δD(CH ₄)	δ ¹³ C(CO ₂)		
XS-07	87.57	0.03	0.21	8.77	0.15	>0.99	0.24	-42.32	-238.27	-12.2	2+8+9	390
XS-13	93.52	0.02	0.34	4.54	0.07	>0.99	0.36	-43.62	-233.66	-12.8	2+8	630
XS-14	93.33	0.05	0.32	4.55	0.07	>0.99	0.34	-41.3	-234.43	-6	2+8+9	601
XS-25	90.47	0.03	0.29	5.95	0.12	>0.99	0.32	-43.85	-235.41	-13.2	2+8+9	482
XS-28	86.19	0.04	0.33	8.98	0.16	>0.99	0.38	-41.45	-224.73	-11.65	2+8+9	345
XS-30	88.47	0.03	0.31	7.05	0.14	>0.99	0.35	-42.24	-222.45	-12.33	2+8	372
Average	89.93	0.03	0.30	6.64	0.12		0.33	-42.46	-231.49	-11.36		

Note: CDMI = $(CO_2)/[(CO_2) + (CH_4)]$

Buried depth is obviously inadequate. The buried depths of XS-14 and XS-13 are greater than 600m. N₂ content is less than 5% in coalbed gas, indicating favourable preservation conditions in this area.

The average N₂ content of non-hydrocarbon components in coalbed gas is 4.8 %, which is relatively large. The nitrogen in coalbed gas is mainly caused by atmospheric and organic factors. The atmospheric nitrogen enters into the coalbed gas reservoir along with groundwater in the form of dissolved gas, so the composition is relatively stable with $(N_2)/(Ar) = 84$. The organic nitrogen is mainly derived from the thermal evolution of nitrogen in organic matter, and $(N_2)/(Ar) \gg 84$. Due to the differences of solubility between nitrogen and argon, $(N_2)/(Ar) = 40$ for the dissolved gas in groundwater [19,20]. It can be seen from Table 1 that $(N_2)/(Ar)$ is between 50~65 with the average being 57 (between

40 and 84), which indicates that the organic and atmospheric nitrogen coexist in the coalbed methane. This further illustrates the good fluidity of groundwater in Tunlan minefield.

As for the perspective of hydrogeology, underground water of Tunlun minefield includes three basal waters: middle Ordovician fissure aquifer, upper carboniferous in limestone of Taiyuan formation aquifer and Shanxi sandstone fissure aquifer. K₃ sandstone, No.2 and No.4 sandstone fissure aquifers impact No.2 coal mine. Sandstone and limestone of Taiyuan formation aquifer consists of L₁, K₂ and L₄ layers of limestone. The top of No.8 coalbed is L₄ limestone. Average thickness of L₄ is 1.80m (Fig.2). Although aquifer exposure poses little impacts on mining coal seam, it is deeply buried with bad aqosity and connectivity. But hydraulic connection exists between group rivers, rainfall and coalbed water, thus forming the basis for secondary biogenic gas.

Coalbed CO₂ was generated during early stages of coalification. With the ongoing process thermal evolution, CH₄ content increased, and CO₂ content declined [21]. In coalbed gas of Tunlun minefield, CO₂ content ranges from 0.21% to 0.34%. Average content is 0.30%. CO₂<5%, which is at a low level. It is less influenced by CO₂ from inorganic source and dissolution of carbonate minerals. It is mostly influenced by decarboxylic reaction with organic macromolecules and organic matters decomposed by bacteria. According to literature research [22], CO₂<5% is another feature of micro-biogenic factor for coalbed gas in Sydney and Bowen basins. According to N₂ content changes, it can be inferred that coalbeds in Tunlun minefield and surface water are closely related. Microbial flora is incorporated to the coalbed to detect CO₂ content, and secondary biogenic gas may exist in Tunlan minefield.

4.2 CARBON ISOTOPE CHARACTERISTICS OF COALBED GAS

Under different parent materials and coal forming environment, the carbon isotopic characteristics of coalbed gas are different. And the carbon isotope fractionation is caused by many physical, chemical and biological factors in later periods, resulting in the great varieties of carbon isotopic characteristics of the current coalbed gas. Carbon is one of

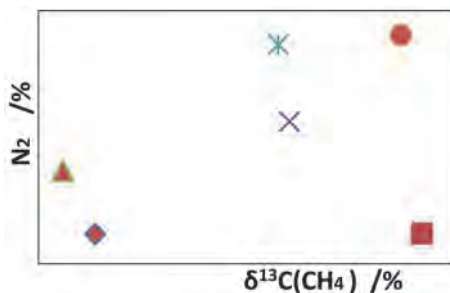


Fig.3 Relational of δ¹³C(CH₄)-N₂ in Tunlun minefield

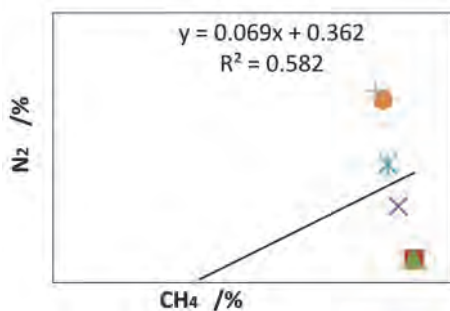


Fig.4 Relational graph of CH₄-N₂ in Tunlun minefield

5. Discussions

5.1 ORIGIN OF METHANE

According to the geochemical parameters including the chemical composition of coalbed gas and methane carbon and hydrogen isotope, origins of the coalbed gas can be classified into primary biogas, secondary biogas, thermal degradation gas, thermal cracking gas and multi-genetic gas [23]. The thermogenic and biogenic methane can be identified by carbon isotopic composition. The primary biogenic methane is mainly formed in the initial stage of peat and low-rank coal thermal evolution, and the secondary biogenic methane can be formed in the high-rank coal [22]. The value of $\delta^{13}\text{C}(\text{CH}_4)$ generated under the microbial action is generally less than -50%. The value of $\delta^{13}\text{C}(\text{CH}_4)$ produced by the reduction of carbon dioxide is in the range of -110%~-60%, and the value of $\delta^{13}\text{C}(\text{CH}_4)$ produced by acetate fermentation is in the range of -65%~-50% [24,25]. The carbon isotope of thermogenic methane is relatively heavy and generally heavier than -50%.

The thermogenic methane is generated when the volatile organic matter rich in hydrogen and oxygen undergoes the physico-chemical changes under certain temperature ($>50^\circ\text{C}$) and pressure. The process of methane production by organic matters in coal or peat under thermal action includes two different mechanisms of formation and corresponding gas generation phases: thermal decomposition and thermal cracking [23]. In the early stage of coalification (R_0 value is within 0.50%~0.80%), the chemical components of the early thermogenic coalbed gas produced from high-volatile bituminous coal contain much moisture such as ethane and propane except methane. In the stage of moisture generation (R_0 value is between 0.60% and 0.80%), the drying coefficient of the coalbed gas is less than 0.8, and the ethane content may exceed 11%. When the R_0 value is between 0.80% and 1.00%, the coal will produce a large amount of thermogenic methane; when the R_0 value is about 1.20%, the coal seam is in the peak of gas generation [26]. The R_0 value of No.8 in Tunlan minefield is 1.1~1.65%, the coalbed gas is in the peak of gas generation and may contain thermogenic gases.

The average carbon isotope of CH_4 in Tunlan minefield is -42.46%, which is higher than the upper limit (-50%) of secondary biogenic gas and is lower than the lower limit (-35%) of thermal genetic gas of Qinshui Basin [7]. The genesis of coalbed methane in Tunlan was analyzed through the relationship between methane hydrogen isotopes and carbon isotopes proposed by Whiticar [27] (Fig.5). The test data of coalbed methane of Tunlan falls in the range of thermal genesis gas. Methane hydrogen isotopes ($\delta\text{D}(\text{CH}_4)$) of coalbed methane in Tunlan minefield ($\delta\text{D}(\text{CH}_4)$) are between -238.27%~-222.45%, which is significantly lower than the range of pyrolysis gas (CH_4) values of Zhengzhuang and Hudi in southern Qinshui Basin (-179.32%~-160.53%) [11], and is included in the $\delta\text{D}(\text{CH}_4)$ value range of the secondary biogenetic coalbed methane of Li Yazhuang in Huozhou

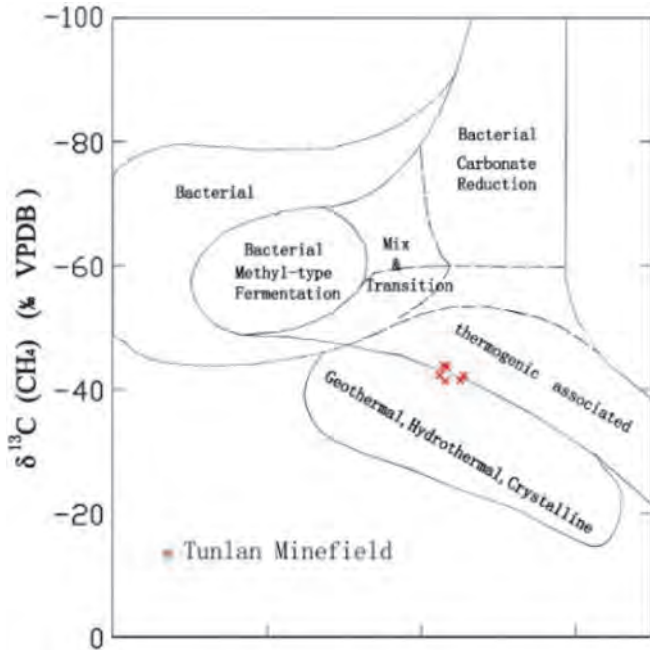


Fig.5 The origin of methane carbon and hydrogen isotopes of the coalbed methane in Tunlan minefield (the base map is cited from literature [27])

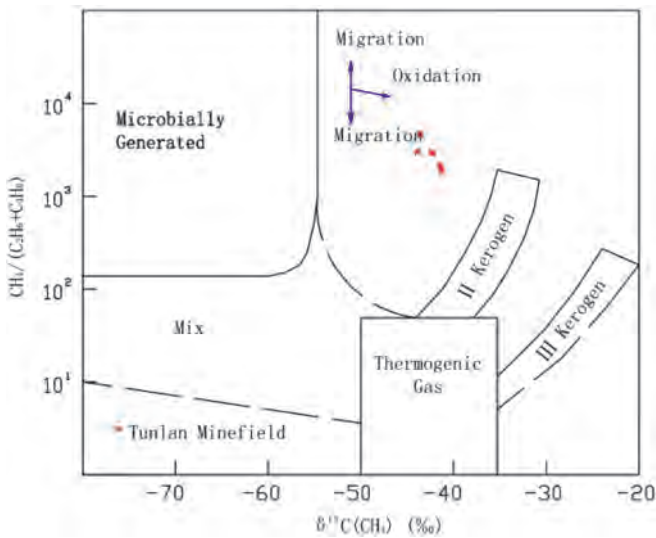


Fig.6 Bernard discrimination diagram of the origin of coalbed methane in Tunlan minefield (the base map is cited from literature [28])

the most important elements of coalbed gas, and almost all the carbon in coalbed gas comes from coal. The carbon isotope ($\delta^{13}\text{C}(\text{CH}_4)$) of coalbed methane Tunlan minefield is within the range of -43.85%~-41.3%, averaging -42.46%. The hydrogen isotopes of methane ($\delta\text{D}(\text{CH}_4)$) is -238.27%~-222.45% with an average value of -231.49%. The carbon isotopes of ethane is -27.74%~-7.61%, the average of which is -21.29%; and the carbon isotope value $\delta^{13}\text{C}(\text{CO}_2)$ of carbon dioxide is -12.8%~-6%, averaging -11.36%.

coalfield (-244%~-215%) [23]. This may show the mixed results of two types of genetic types of coalbed methane. According to the Bernard (Fig.6) of the relationship between $\delta^{13}\text{C}(\text{CH}_4)$ and $C_1/(C_1+C_2)$, the coalbed methane in Tunlan has undergone secondary transformation, which is not purely thermogenic gas.

5.2 ORIGINS OF CARBON DIOXIDE IN THE COALBED GAS

Carbon dioxide in coalbed gas varies in contents and is soluble in water. When the carbon dioxide content is less than 15%, it is considered to be organogenic; and when the concentration is more than 60%, it is inorganic genetic [29]. The average carbon dioxide content in the coalbed gas of Tunlan minefield is 0.30%, indicating organic genesis.

The value of $\delta^{13}\text{C}(\text{CO}_2)$ in coalbed gas of Tunlan minefield is within the range of -13.2% ~-6.0%, averaging -11.36%. Among the test samples taken from Tunlan minefield of Xishan in Taiyuan, other than XS-14 with the $\delta^{13}\text{C}(\text{CO}_2)$ value of -6.0%. The test results of carbon dioxide carbon isotope in the rest of samples is within the range of -13.2% ~-11.65%, averaging -11.36%. The test results of carbon dioxide carbon isotope of Tunlan minefield are significantly heavier than the range of carbon dioxide carbon value of Sydney basin and Bowen basin in Australia (-15.5%~+16.7%) [22] and in Upper Silesian basin in Poland (-27.2% ~ -2.8%) [28]. Therefore, carbon dioxide of the coalbed gas in the Tunlan minefield should be the residual secondary biogas.

The carbon isotopic composition of carbon dioxide from different sources may be different. The value of $\delta^{13}\text{C}(\text{CO}_2)$ of organic genesis is less than -10%; the inorganic genetic $\delta^{13}\text{C}(\text{CO}_2)$ is greater than -8% [29], the $\delta^{13}\text{C}(\text{CO}_2)$ relative to the secondary biogas is in the range of -40%~+20% [24]; and the carbon isotope value of carbon dioxide from thermal cracking of coal do not exceed 0.15% [30]. The value of $\delta^{13}\text{C}(\text{CO}_2)$ in coalbed gas of Tunlan minefield is within the range of -13.2% ~-6.0%, averaging -11.36%. Therefore, carbon dioxide of the coalbed gas in the Tunlan minefield should be the secondary biogas and thermal cracking gas.

5.3 THE RELATION BETWEEN ORIGINS OF METHANE AND DIOXIDE CARBON IN THE COALBED GAS

The genetic analysis can also be carried out on the basis of the carbon isotope values of CH_4 and CO_2 [10]. The carbon isotope values of CH_4 and CO_2 of Tunlan minefield are all in the thermogenesis area, but the carbon isotope values of CH_4 and CO_2 have positive correlation. According to existing researches [10,12]. The carbon isotopic values of CH_4 and CO_2 have a positive correlation, and secondary biogenic gas exists at the surface of coalbed methane. The formation of secondary biogas can be determined by the formula with $\delta^{13}\text{C}(\text{CH}_4)$ and fractionating factor $\alpha(\text{CO}_2-\text{CH}_4)$ of $\delta^{13}\text{C}(\text{CO}_2)$.

$$\alpha(\text{CO}_2-\text{CH}_4) = (1000 + \delta^{13}\text{C}(\text{CO}_2)) / (1000 + \delta^{13}\text{C}(\text{CH}_4)) \dots (1)$$

When $\alpha(\text{CO}_2-\text{CH}_4)$ is 1.03~1.06, indicating that secondary biogenic gas is formed by methyl fermentation. When $\alpha(\text{CO}_2-$

$\text{CH}_4)$ 1.06~1.09, indicating that secondary biogenic gas is formed by reduction of carbon dioxide. According to Eq(1), the isotopic fractionation factor $\alpha(\text{CO}_2-\text{CH}_4)$ of the sample from Tunlan is 1.03~1.04, indicating it is methyl fermentation.

The value of $\delta^{13}\text{C}$ reflects the mass percentage of methane produced by reduction of CO_2 . When the mass percentage of methane is 50%, $\delta^{13}\text{C}$ is about +2%; when it is 30%, $\delta^{13}\text{C}$ is around -15% [31]. Since the average of $\delta^{13}\text{C}$ of the six samples is -11.36%, it can be referred to that the percentage of the secondary biogas formed by bacterial degradation is about 35%.

6. Conclusions

- (1) The average volume fraction of CH_4 content of coalbed methane in Tunlan minefield in Xishan coalfield is 86.19%~93.52%, and the average content is 89.93%. The content of ethane is few, which is 0.02%~0.05%, and the average is 0.03%. The nonhydrocarbon gases are mainly nitrogen, carbon dioxide and argon, and the volume content is 4.54%~8.98%, 0.21%~0.34% and 0.07%~0.16% respectively. Their average values are 6.64%, 0.30% and 0.12%. The drying coefficient is more than 0.99, which is extremely dry gas, and CDMI is 0.24%~0.38%.
- (2) Methane carbon isotopes of coalbed methane in the Tunlan minefield in Xishan coalfield is -43.85%~-41.3%, and the average is -42.46‰; the hydrogen isotopes of methane is -238.27%~-222.45% with an average value of -231.49‰; the carbon isotopes of ethane is -27.74%~-7.61%, the average of which is -21.29%; the carbon isotopes of carbon dioxide is -12.8%~-6.0% with an average number of -11.36%.
- (3) Coalbed methane in Tunlan minefield has undergone secondary transformation, which is mainly dominated by thermal degradation of coal. Secondary biogenic gas CH_4 exists, which means it is mixed genetic coalbed methane, and the ratio of secondary biogas gas is about 35%.

Acknowledgments

This paper is supported by the generous funding by Shanxi Coalbed Gas United Fund (Project No. 2012012003 and 2015012015), National Natural Science Fund (Project No 41372215), and the Education Reform Program of North University of China (2016). My thanks also go to Dr. Tian Yongdong, Engineer Wu jie and Engineer Li Jin from the Key Laboratory of Coal and Coalbed Gas Simultaneous Extraction, Shanxi Province and Dr. Li Zhongping from Lanzhou Center for Oil and Gas Resources, Institute of Geology and Geophysics, CAS for their tremendous support during sampling and testing.

References

1. Duan, Y., Sun, T. and Liu, J. F. (2010): "Thermal simulation experiment and application of staged evolution of coalbed

- methane carbon isotope.” *Acta Sedimentologica Sinica*, vol.28, no. 2, pp. 401-40.
2. Song, Y., Liu, S. B. and Hong, F. (2012): “Geochemical characteristics and genesis of coalbed methane in China.” *Acta Petrolei Sinica*, vol. 33, pp. 99-106.
 3. Hou, Q. L., Li, H. J. and Fan, J. J. (2012): “Structure and coalbed methane occurrence in tectonically deformed coals.” *Science China Earth Sci.*, vol. 55, no. 11, pp. 1755-1763.
 4. Zhang, J. B. and Tao, M. X. (2000): “Geological significances of coalbed methane exploration.” *Acta Sedimentologica Sinica*, vol. 18, no. 4, pp. 611-614.
 5. Qin, Y., Tang, X. Y. and Ye, J. P. (2000): “Characteristics and Origins of Stable Carbon Isotope in Coalbed Methane of China.” *Journal of China University of Mining & Technology*, vol. 29, no. 2, pp. 113-119.
 6. Meng, Z. P., Zhang, J. X. and Liu, H. (2014): “Relationship between the methane carbon isotope and gas-bearing properties of coal reservoir.” *Journal of China Coal Society*, vol. 39, no. 8, pp. 1683-1690.
 7. Li, J. J., Zhang, J. L. and Wang, B. Y. (2016): “Characteristics and origin of $^{13}\text{C}(\text{CH}_4)$ in coal-bed gas in southern Qinshui basin.” *Oxidation Communications*, vol. 39, no. 4-III, pp. 3835-3851.
 8. Qin, S. F., Tang, X. Y. and Song, Y. (2006): “Distribution characteristics and fractionation mechanism of coalbed methane carbon isotope.” *Science China: D Earth Sciences*, vol. 36, no. 12, pp. 1092-1097.
 9. Song, Y., Qin, S. F. and Zhao, M. J. (2007): “Two key geological factors controlling the coalbed methane reservoirs in China.” *Natural Gas Geoscience*, vol. 18, no. 4, pp. 545-553.
 10. Golding, S. D., Boreham, C. J. and Esterle, J. S. (2013): “Stable isotope geochemistry of coalbed and shale gas and related production waters: A Review.” *International Journal of Coal Geology*, vol. 120, pp. 24-40.
 11. Li, J. J., Bai, P. K. and Mao, H. P. (2014): “Analysis of geochemistry characteristics and its origin of CBM in Zhengzhuang and Hudi blocks.” *Journal of China Coal Society*, vol. 39, no. 9, pp. 1802-1811.
 12. Hamilton, S. K., Golding, S. D. and Baublys, K. A. (2014): “Stable isotopic and molecular composition of desorbed coal seam gases from the Walloon Subgroup, eastern Surat Basin, Australia.” *International Journal of Coal Geology*, vol. 122, pp. 21-36.
 13. Zhao, M. J. and Zhang, S. C. (2004): “Main factors for controlling geochemical characteristics of natural gas in the Tarim Basin.” *Chinese Journal of Geology*, vol. 39, no. 4, pp. 507-516.
 14. Zhao, M. J., Song, Y. and Su, X. B. (2005): “Differences for geochemical controlling factors between coalbed and conventional natural gases.” *Petroleum Exploration and Development*, vol. 32, no. 6, pp. 21-24.
 15. Guan, Y. B. and Li, H. M. (2001). “The structural framework and evolution of taiyuan area.” *Journal of Liaoning Technical University (Natural Science)*, vol.20, no.1, pp.32-35.
 16. Liu, H.L., Wang, H.Y. and Zhao, G.L. (2005). “Influence of the tectonic thermal events in Yanshan epoch on coalbed methane enrichment and high productivity in Xishan coalfield in Taiyuan.” *Natur. Gas Ind.*, vol.25, no.1, pp. 29-32.
 17. Wang, B., Jian, G. B. and Guo, Z. B. (2007): “Coalbed methane reservoir-forming characteristics of Xishan coalfield, Qin shui Basin.” *Natural Gas Geoscience*, vol.18, no.4, pp. 565-567.
 18. Hu, G. Y., Guan, H. and Jiang, D. W. (2012): “Analysis of conditions for the formation of a coal methane accumulation Qinshui coal methane field.” *Geology in China*, vol. 31, no. 2, pp. 213-217.
 19. Maksimov, S. P., Muller, E. P. and Botneva, T. A. (1975): “Origin of high nitrogen gas pools.” *International Geology Review*, vol. 18, no. 5, pp. 551-556.
 20. Marty, B., Criaud, A. and Fouillac C. (1988): “Low enthalpy geothermal fluids from the Paris Sedimentary Basin: Characteristics and origin of gases.” *Geothermics*, vol. 17, pp. 419-453.
 21. Ju, Y. W., Li, Q. G. and Yan, Z. F. (2014): “Origin types of CBM and their geochemical research progress.” *Journal of China Coal Society*, vol. 39, no. 5, pp. 806-815.
 22. Smith, J. W. and Pallasser, R. J. (1996): “Microbial origin of Australian coalbed methane.” *AAPG Bulletin*, vol. 80, no. 6, pp. 891-897.
 23. Tao, M. X., Wang, W. C. and Duan, Y. (2014): “Origin and types of coalbed methane and its contribution to resources.” *Beijing: Science Press*, pp. 1-149.
 24. Whitcar, M. J., Faber, E. and Schoell, M. (1986): “Biogenic methane formation in marine and freshwater environments: CO₂ reduction vs. acetate fermentation-isotope evidence.” *Geochim Cosmochim Acta*, vol. 50, pp. 693-709.
 25. Xie, S. C., Yang, H. and Luo, G. M. (2012): “Geomicrobial functional groups: A window on the interaction between life and environments.” *Chinese Science Bulletin*, vol. 57, no. 1, pp. 3-22.
 26. Scott, A.R., Kaiser, W.R., Ayers, W.B. (1994): “Thermogenic and secondary biogenic gases, San Juan Basin Colorado and New Mexico-implications for coalbed gas producibility.” *AAPG Bulletin*, vol. 78, no. 8, pp. 1186-1209.
 27. Whitcar, M. J. (1999): “Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane.” *Chemical Geology*, vol. 161, pp. 291-314.
 28. Kotarba, M. J. (2001): “Composition and origin of coalbed gases in the Upper Silesian and Lublin basins.” *Poland Organic Geochemistry*, vol. 32, no. 1, pp. 163-180.
 29. Dai, J. X., Shi, X. and Wei, Y. Z. (2001): “Summary of the inorganic origin theory and the abiogenic gas pools (fields).” *Acta Petrolei Sinica*, vol. 22, no. 6, pp. 5-10.
 30. Song, Y., Liu, S. B. and Zhang, Q. (2012): “Coalbed methane genesis, occurrence and accumulation in China.” *Petroleum Science*, vol. 9, no. 3, pp. 269-280.
 31. Jones, D. M., Head, I. M. and Gray, N. D. (2008): “Crude oil biodegradation via methanogenesis in subsurface petroleum reservoirs.” *Nature*, vol.451, pp. 176-180.